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BCS Primer: A Guide to Computational Methods in Superconductivity Theory

by

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**BCS Primer: A Guide to Computational Methods
in Superconductivity Theory**

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ABSTRACT

Because of the recent revival of interest in superconductivity, we have felt that a pedagogical, yet concise review of the fundamental ideas of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity is timely. We discuss the basic ideas of the BCS theory and list the formulae for the thermodynamic quantities of this theory in the usual real-time representation. We also represent these formulae in the alternate imaginary-time representation, which makes "hands-on" numerical evaluation of the thermodynamic quantities of interest readily accessible. Finally, we point out the limitations of the BCS theory and describe some of its proposed extensions for describing the behavior of some of the new, unconventional superconductors.



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The discovery of "high-temperature" superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ by J. Georg Bednorz and K. Alex Müller (1) in late 1986 has inspired intense experimental and theoretical work worldwide in all areas of superconductivity. The study of superconductivity will therefore, no doubt become a vital part of the education of the next generation of scientists. With this perspective in mind, we shall attempt to provide a concise survey of the important ideas of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity (2) as a first step towards understanding more advanced concepts in superconductivity theory which have arisen with the advent of the "high-temperature" and other unconventional superconducting materials. In addition to providing a cursory development of the BCS theory of superconductivity, we also give a compilation of formulae which describe the thermodynamic properties of a BCS superconductor. Our emphasis here is on enabling the reader to get to the problem-solving stage as directly as possible. We refer the reader desiring a more rigorous treatment to the various texts on superconductivity theory (3). A very useful resource of references on various aspect of superconductivity can be found in Ginzberg (4). We include this report with a discussion of the limitation of the BCS theory and a survey of the extensions of it which have been proposed to treat unconventional superconducting materials such as the heavy-fermion and "high- T_c " superconductors.

BCS THEORY

In this section we briefly discuss the key points of the BCS theory following the treatment by Leggett (5). The important first step towards formulating a theory of superconductivity was taken by Cooper (6). He considered the idealized case of a pair of electrons in a metal, one of momentum k and spin \uparrow and the other of momentum $-k$ and spin \downarrow , which at

temperature $T = 0$ are coupled by the effective attractive interaction $g < 0$. The coupled or bound electron pair (the Cooper pair) is of lower energy than a separated electron pair, provided they interact in the presence of a filled Fermi sea composed of the remaining $N-2$ electrons. That is the momentum of the paired state, k , is greater than the Fermi momentum k_F and the Fermi sea blocks the electron pair from being scattered to states below k_F . In analogy to the single-pair case, one might think that an ensemble of many such pairs might lower the energy still further. Bardeen, Cooper and Schrieffer (2) showed that this is indeed the case; the new state so formed is called the superconducting state.

The BCS ground state is usually referred to as a spin-singlet, even-parity s-state. This simply means that the total spin S of the pair with individual spin components $+\frac{1}{2}$ and $-\frac{1}{2}$ is $S = 0$, and that the relative orbital angular momentum of the pair is $l = 0$. Superconducting states can be formed for other values of l and, in analogy to atomic orbitals, are labeled as p-wave, d-wave states, etc. We shall comment on these extensions later.

The effective interaction g between the Cooper pairs must be attractive to form the superconducting state, i.e., the coupling energy must be greater than the Coulomb repulsion between the pair. The mechanism by which electrons pair establishes the genre of the superconductor. BCS superconductors are characterized by an electron-phonon mechanism. An electron passing through the lattice of positive ions of a metal will draw these ions toward it, i.e., polarize the lattice. Due to the large mass of the ions compared to the electron, the lattice remains polarized for some time after the electron has passed. Therefore, a second electron can be attracted to the net positive charge and becomes effectively coupled to the

first electron. Experimental measurements of quantities such as electrical resistivity, thermal conductivity and the superconducting transition temperature can be used to determine the strength of the electron-phonon interaction.

We shall now briefly review the method of second quantization, which will help us in describing the mathematics of superconductivity theory. A non-interacting N -particle system is characterized by wave functions $\phi_i(r_i, s_i)$, $i = 1, 2, \dots, N$, with r_i denoting positions and s_i the spins of the particles. The wave functions form a complete orthonormal basis set of which the states of the system are composed. In the second-quantized representation one does not specify the wave functions of the system of particles; instead, the particle numbers n_1, n_2, \dots in these states are specified as the system variables. The particle numbers are the eigenvalues of the number operators \hat{n}_i given by $\hat{n}_i = c_i^\dagger c_i$, where c_i^\dagger is the creation operator for state i and c_i is the corresponding annihilation operator. The operator c_i^\dagger acting on a state i with n_i particles in it, increases the number of particles to (n_i+1) , whereas the operator c_i acting on the same state decreases the number of particles to (n_i-1) . If we are dealing with fermions, such as electrons, the creation and annihilation operators obey anticommutation relations such as $c_i c_i^\dagger + c_i^\dagger c_i = 1$, $c_i c_j^\dagger + c_j^\dagger c_i = 0 (i \neq j)$, etc., reflecting the antisymmetry of the complete wave function of the system. The antisymmetry of the total wave function puts restrictions on the possible values of the particle numbers n_i (i.e., the Pauli Exclusion Principle).

We shall treat the BCS theory at $T = 0$ first (the ground-state problem). Let us write the wave function of the system Ψ as a product of pair states given by

$$\Psi = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^{\dagger} c_{-\mathbf{k}\downarrow}^{\dagger}) |0\rangle \quad (1)$$

Here $|0\rangle$ is the uncorrelated vacuum state, $c_{\mathbf{k}\uparrow}^{\dagger} c_{-\mathbf{k}\downarrow}^{\dagger}$ is the creation operator for the superconducting pair state, $v_{\mathbf{k}}$ is the complex probability amplitude for the electron pair state to be occupied, and $u_{\mathbf{k}}$ is the complex probability amplitude for the pair state to be unoccupied. The total probability for a state at \mathbf{k} must be 1, i.e., $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$. Suppose initially that the pair state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ is occupied and that the state $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$ is unoccupied where \mathbf{k}' and \mathbf{k} differ by momentum \mathbf{q} . The probability amplitude that the system is in the initial state is $v_{\mathbf{k}} u_{\mathbf{k}'}$. If there is a scattering process in which the first state becomes unoccupied and the second state becomes occupied, the probability amplitude for the transition becomes $u_{\mathbf{k}}^* v_{\mathbf{k}'}^* v_{\mathbf{k}} u_{\mathbf{k}'}$. Since eq. 1 implies that the superconducting state is a superposition of states containing different numbers of particles, we must work in the grand canonical ensemble for which the energy operator is

$$K = H - \mu N = (T+V) - \mu N \quad (2)$$

$$\text{with } T = \sum_{\mathbf{k}, \alpha} \epsilon_{\mathbf{k}} c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}\alpha}, \quad N = \sum_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}\alpha} \quad \text{and} \quad V = -\frac{1}{2}|g| \sum_{\mathbf{k}\mathbf{k}'} \sum_{\alpha, \beta} c_{\mathbf{k}'\alpha}^{\dagger} c_{-\mathbf{k}'\beta}^{\dagger} c_{-\mathbf{k}\beta} c_{\mathbf{k}\alpha}$$

Here μ is the chemical potential, T is the kinetic energy, and V is the potential energy containing the effective interaction g , discussed earlier. It is assumed that g is independent of the frequency of vibration of the ions of the lattice. The spin indices α and β can each be \uparrow or \downarrow , and N is the total number of electrons in the system which is fixed by the chemical potential μ . The characteristic energy of vibration of ions (the Debye

energy $\hbar\omega_D$) is assumed to be much higher than any excitation energy of the electrons being considered. If the wave function of the pair state has the form given by eq. 1, then, intuitively, the average quantity $\langle T - \mu N \rangle$ is

$$\langle T - \mu N \rangle = \sum_{\mathbf{k}} 2 \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 \quad (3)$$

The factor 2 arises because there are two electrons in the pair. The quantity $\xi_{\mathbf{k}}$ is simply the kinetic energy of an electron measured with respect to the chemical potential ($\xi_{\mathbf{k}} = \epsilon_{\mathbf{k}} - \mu$). To get the average potential energy $\langle V \rangle$, we restrict ourselves to taking averages of pairs of operators (mean-field approximation) such as

$$\langle c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger \rangle \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle = (u_{\mathbf{k}}, v_{\mathbf{k}}^*) (u_{\mathbf{k}}^*, v_{\mathbf{k}}) = F_{\mathbf{k}}^*, F_{\mathbf{k}} \quad (4)$$

The non-zero value of the particular average given above differentiates the superconducting state from the normal, metallic state, the averages of other combinations of operator pairs being the same as in the normal state.

So finally, the average energy can be written as

$$\langle \mathcal{H} \rangle = \sum_{\mathbf{k}} 2 \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 - |g| \sum_{\mathbf{k}, \mathbf{q}} F_{\mathbf{k}}^* F_{\mathbf{k}-\mathbf{q}} \quad (5)$$

It is convenient to express $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ in terms of a complex quantity $\Delta_{\mathbf{k}}$ defined by

$$v_{\mathbf{k}} = \Delta_{\mathbf{k}} / D_{\mathbf{k}} \quad \text{and} \quad u_{\mathbf{k}} = (E_{\mathbf{k}} + \xi_{\mathbf{k}}) / D_{\mathbf{k}} \quad (6)$$

with $E_k = \sqrt{|\Delta_k|^2 + \xi_k^2}$, and $D_k = \sqrt{|\Delta_k|^2 + (E_k + \xi_k)^2}$, such that

$$|u_k|^2 + |v_k|^2 = 1 \text{ and } F_k = u_k^* v_k = \Delta_k / 2E_k. \quad (7)$$

To find the ground-state energy, we minimize eq. 5 with respect to F_k^* . By noting that the first term on the RHS of eq. 5 can be written as $2 \sum_k \int \Delta_k dF_k^*$ (apart from a constant) (5), the required minimization gives

$$\Delta_k = |g| \sum_{k'} F_{k'} = 2|g| \sum_{k'} \Delta_{k'} / (2E_{k'}) \quad , \quad \text{with } k' = k - q \quad (8)$$

Equation 8 is the famous BCS self-consistency relation, at $T = 0$, which implicitly defines the complex gap function Δ_k . This equation, when solved numerically, admits to a non-zero solution for the gap function Δ_k . In the normal state the function F_k defined by eq. 7 is identically zero, implying that $\Delta_k = 0$. Thus Δ_k serves as the complex order parameter of the theory of superconductivity. For the sake of simplicity we shall assume that Δ_k is independent of k and drop its k -label. However, in the case where the gap function can change with position, the k -label, as we shall see, is important.

The physical interpretation of $|\Delta|^2$, introduced in eq. 6, is that of an energy gap. The relation $E_k = \sqrt{\xi_k^2 + |\Delta|^2}$ implies that there is a gap, Δ , in the energy spectrum of a superconductor. This gap appears because a single pair cannot be broken without a finite expenditure of energy. Thus the energy gap originates from the fact that there is a binding energy between electrons in a Cooper pair. The elementary excitations of the ground pair (GP) state are of two kinds. The first kind can be formed by breaking up

the pair, i.e., only one of the two particles occupies the pair state. Therefore, there is a single particle in the $k\uparrow$ or in the $-k\downarrow$ state, each having kinetic energy ξ_k (relative to μ), but losing the pairing energy (i.e., $F_k = 0$). This type of excitation will be called the broken pair (BP) state. The second kind of excitation, called the excited pair (EP) state, can be formed in a manner similar to eq. 1, the only difference being that the new probability coefficients for this state are so chosen that this state is higher in energy and is orthogonal to the state given by eq. 1. The GP, BP and EP states are analogous to the bonding, nonbonding and antibonding states of molecular hydrogen. It can be shown that the excitation energies of a single BP state (there are two such states) and the EP state relative to the ground pair (GP) state are (for details see Leggett (5)) $E_{BP} - E_{GP} = E_k$ and $E_{EP} - E_{GP} = 2E_k$.

The concepts of the three states, GP, BP and EP, help us to generalize the BCS theory to finite temperatures ($T > 0$). The quantities u_k , v_k , Δ_k , E_k and F_k now become implicitly dependent on temperature. The probabilities of occurrence of these states, are given by

$$P_{GP} = n^{-1}, P_{BP} = n^{-1} \exp[-\beta E_k], P_{EP} = n^{-1} \exp[-2\beta E_k], \quad (9)$$

with $n = (1 + 2 \exp[-\beta E_k] + \exp[-2\beta E_k])$ where $\beta = 1/T$ (using units in which Boltzmann's constant is unity). The quantity F_k in eq. 7 is generalized to

$$F_k = u_k^* v_k (P_{GP} - P_{EP}) = (\Delta/2E_k) \tanh(\beta E_k/2) \quad (10)$$

Notice that the BP state does not contribute to eq. 10, since the amplitude factor $u_k^* v_k$ is zero for this state.

THERMODYNAMIC PROPERTIES

The Real-Time Representation

The evaluation of thermodynamic quantities within BCS theory can be performed in two ways. The first method, called the real-time representation, follows along the lines of the theory outlined in the previous section for $T = 0$. The second method, called the imaginary-time representation, will be discussed in the next section. In the real-time representation, the time dependence of creation and annihilation operators involves exponential terms of the form $\exp(\pm iKt)$, where K is the energy operator defined in eq. 2. If the wave vectors, k , are closely spaced, forming a quasi-continuous spectrum near the Fermi surface, then we can replace the sum over k by an integral over energy through the correspondence

$$\sum_{\mathbf{k}} \longrightarrow N(0) \int_{-\omega_D}^{\omega_D} d\xi_{\mathbf{k}} , \quad (11)$$

where $N(0)$ is the density of states (i.e., number of states per unit energy interval) per single spin evaluated at the Fermi energy (i.e., $\mu=0$), and ω_D is the Debye frequency. The self-consistency relation, eq. 8, can now be generalized with the help of eq. 10 to give

$$\Delta = |g| \sum_{\mathbf{k}} F_{\mathbf{k}} - \lambda \int_{-\omega_D}^{\omega_D} d\xi_{\mathbf{k}} [\Delta/2E_{\mathbf{k}}] \tanh[E_{\mathbf{k}}/2T] , \quad (12)$$

where $\lambda = N(0)|g|$. At the transition temperature ($T = T_c$), $\Delta = 0$, so that eq. 10 reduces to

$$1 = \lambda \int_{-\omega_D}^{\omega_D} d\xi_k (2\xi_k)^{-1} \tanh(\xi_k/2T_c) \quad , \quad (13)$$

$$\text{or} \quad \lambda^{-1} = \ln[\Gamma\omega_D(2\pi T_c)^{-1}] \quad , \quad (14)$$

where $\ln\Gamma$ is equal to Euler's constant (0.577). Rearranging eq. 14 yields the transition temperature as

$$T_c = 1.135 \omega_D \exp(-1/\lambda) \quad . \quad (15)$$

At $T = 0$, $\Delta = \Delta_0$ and eq. 12 can be directly solved to give

$$\lambda^{-1} = \int_0^{\omega_D} d\xi (\xi^2 + |\Delta_0|^2)^{-1/2} \approx \ln(2\omega_D/\Delta_0) \quad (\because \omega_D/\Delta_0 \gg 1) \quad . \quad (16)$$

$$\text{Hence,} \quad \Delta_0 = 2\omega_D \exp(-1/\lambda) \quad . \quad (17)$$

By eliminating λ from eqs. 15 and 17 we get $(\Delta_0/T_c) = 1.76$ which is a universal constant of the BCS theory, being independent of the parameters of a particular material such as the density of states and the coupling constant, g . For temperatures $0 < T < T_c$ eq. 12 is solved by eliminating λ and ω_D through the use of eqs. 15 and 17 and through the use of the transformation $\tanh(x/2) = 1 - 2\exp(-x)/[1 + \exp(-x)]$. Equation 12 is thus divided into two terms, the latter being convergent (i.e., integrable from the limits 0 to ∞). We have found that a 15-point Gauss-Laguerre quadrature (7) can be readily applied to solve eq. 12, and is particularly accurate at low temperatures where $\omega_D/T \gg 1$. Numerical solutions of eq. 12

become quite inaccurate, however, near T_c since one has to determine a small quantity, Δ , by subtracting two large numbers. The imaginary-time-representation treatment avoids this problem and is much simpler to use in practice.

Having obtained the temperature-dependent gap function $\Delta(T)$, as given above, we can now calculate the free energy difference $F_s - F_n < 0$ of the superconducting state relative to the normal state. Noting that $\langle V \rangle = -\Delta \sum_{\mathbf{k}} F_{\mathbf{k}}^*$, we can write (5)

$$F_s - F_n = \langle V \rangle + \sum_{\mathbf{k}} [2\Delta F_{\mathbf{k}}^* - 2 \int F_{\mathbf{k}}^* d\Delta] = \sum_{\mathbf{k}} (\Delta F_{\mathbf{k}}^* - 2 \int F_{\mathbf{k}}^* d\Delta) \quad (18)$$

$$= -\frac{1}{2} N(0) |\Delta|^2 - N(0) \int_{-\omega_D}^{\omega_D} d\xi_{\mathbf{k}} \int_0^{\Delta} x dx (x^2 + \xi_{\mathbf{k}}^2)^{-1/2} \tanh(\sqrt{x^2 + \xi_{\mathbf{k}}^2}/2T) ,$$

$$= -\frac{1}{2} N(0) |\Delta|^2 - 2T N(0) \int_{-\omega_D}^{\omega_D} d\xi_{\mathbf{k}} \ln[\cosh(E_{\mathbf{k}}/2T)/\cosh(\xi_{\mathbf{k}}/2T)] .$$

Equation 18 also gives the value of the thermodynamic critical field H_c , since $F_n - F_s = H_c^2/(8\pi)$. The entropy of the superconducting state at temperature T is given by

$$S_s = - \sum_{\mathbf{k}} (P_{GP} \ln P_{GP} + 2 P_{BP} \ln P_{BP} + P_{EP} \ln P_{EP}) \quad (19)$$

$$= N(0) \int_{-\omega_D}^{\omega_D} d\xi_{\mathbf{k}} \left\{ E_{\mathbf{k}} [1 - \tanh(E_{\mathbf{k}}/2T)]/T + 2 \ln[1 + \exp(-E_{\mathbf{k}}/T)] \right\} .$$

The specific heat at constant volume, C_s , of the superconductor is easily calculated from eq. 19 by the formula

$$C_s = T \left(\frac{dS}{dT} \right) = N(0) \int_{-\omega_D}^{\omega_D} d\xi_k \frac{1}{2} \left\{ \frac{E_k^2}{T^2} - \left(\frac{E_k}{T} \right) \cdot \frac{dE_k}{dT} \right\} \operatorname{sech}^2 \frac{\beta E_k}{2} . \quad (20)$$

It is useful to compare $C_s(T)$ above with $C_n(T_c)$, the specific heat of the normal state at T_c . Since $C_n(T) = \gamma T$, where $\gamma = 2\pi^2 N(0)/3$ is the Sommerfeld constant, we have

$$\begin{aligned} \frac{C_s(T)}{\gamma T_c} &= 3(2\pi^2)^{-1} (\Delta/T_c)^3 (T_c/T)^2 \sum_{n=0}^{\infty} (-1)^{n(n+1)} [K_3(x_n) + 3K_1(x_n)] \\ &\quad - 3(2\pi^2)^{-1} \left(\frac{1}{T_c} \frac{d\Delta^2}{dT} \right) Y(T) , \end{aligned} \quad (21)$$

$$\text{with } Y(T) = \int_0^{\infty} d\xi_k (1/2T) \operatorname{sech}^2(E_k/2T) = 1 - \alpha , \quad (22)$$

where $x_n = (n+1)\Delta/T$ and $\alpha^{-1} = [1 - (T \frac{d\Delta^2}{dT}) / (2\Delta^2)]$.

In obtaining eq. 21 we have used the integral representation of the modified Bessel function $K_\nu(x)$ and the identity $\operatorname{sech}^2(x/2) = 4 \sum_{n=0}^{\infty} (-1)^{n(n+1)} \times \exp[-(n+1)x]$. The temperature-dependent quantity $Y(T)$ is called the Yosida function and gives the spin susceptibility of the superconductor. The specific form of $Y(T)$ in eq. 22 was obtained from the discussion on the electromagnetic properties of the superconducting state in the original BCS

paper (2); this term was neglected in (8). The low- and high-temperature limits of these quantities are discussed in the Appendix; numerical values of the thermodynamic quantities over the entire temperature range are given in Rickayzen (9).

The Imaginary-Time Representation

In contrast to the previous section, one can think of temperature as an "imaginary time" τ by writing the Boltzmann factor as $\exp(-\hat{H}/T) = \exp(i\hat{H}\tau)$ with $\tau = i/T$, where τ is defined over a range from 0 to $1/T$. The variable conjugate to τ is called the Matsubara frequency, ω_n . In the imaginary-time representation all thermal averages are expanded in a Fourier series in ω_n (in contrast to the Fourier integrals of the previous section). The antisymmetry of the fermion wavefunction imposes the constraint that $\omega_n = \pi T(2n+1)$ with $n = 0, \pm 1, \pm 2, \dots$. We can express the formulae of the previous section as a series in ω_n very elegantly by the method of analytic continuation discussed in (10).

Let $f(\omega) = [1 + \exp(\omega/T)]^{-1}$ be the Fermi distribution function for a state of energy ω at temperature T , with poles located at $\omega = \pm i\omega_n$. Suppose we wish to evaluate the integral $\oint d\omega f(\omega) F(\omega)$ around a contour which encloses only the poles of $f(\omega)$ but not the poles of the arbitrary function $F(\omega)$. Then it can be shown that

$$\oint d\omega f(\omega) F(\omega) = -2\pi iT \sum_{\omega_n} F(i\omega_n) \quad (23)$$

As a practical application of eq. 23 consider the self-consistency equation,

eq. 12. Since the integrand is an even function of ξ_k , we can replace

$\int_{-\omega_D}^{\omega_D} d\xi_k$ by $2 \int_0^{\omega_D} d\xi_k$. By changing the integration variable from ξ_k to E_k one obtains

$$1 = \lambda \int_0^{\sqrt{\omega_D^2 + |\Delta|^2}} dE_k (E_k^2 - |\Delta|^2)^{-1/2} \tanh(E_k/2T) \quad (24)$$

We can write $\tanh(E_k/2T) = f(E_k)[\exp(E_k/T) - 1]$ and use eq. 23 [note that $\exp(i\omega_n/T) = -1$] to get

$$1 = 2\pi\lambda T \sum_{\omega_n > 0}^{\omega_D} [\omega_n^2 + |\Delta|^2]^{-1/2}, \quad \omega_n = \pi T(2n+1) \quad (25)$$

At $T = T_c$, $\Delta = 0$ so that we get from eq. 25

$$1 = \lambda \sum_{n=0}^{\tilde{n}_D} 1/(n + 0.5), \quad \tilde{n}_D = \text{NINT}[\omega_D(2\pi T_c)^{-1} - 0.5] \quad (26)$$

Here NINT stands for the nearest integral part of the quantity inside the square brackets. As $\tilde{n}_D \rightarrow \infty$, the RHS of eq. 26 is logarithmically divergent, hence the need to truncate the sum at the Debye number \tilde{n}_D associated with the Debye frequency ω_D at T_c . For large \tilde{n}_D , the series on the RHS of eq. 26 can be evaluated (7) and precisely gives the familiar eq. 14. In order to solve for $\Delta(T)$ as a function of temperature, we note that eq. 26 can be rewritten as

$$\lambda^{-1} = \ln(\tau) + \sum_{n=0}^{n_D} 1/(n+0.5) \quad , \quad \tau = T/T_c \quad . \quad (27)$$

Eliminating λ from eq. 21 and 27, we obtain the self-consistency condition

$$\ln \tau + \sum_{n=0}^{n_D} [(n+0.5)^{-1} - 2\pi T(\omega_n^2 + |\Delta|^2)^{-1/2}] = 0 \quad . \quad (28)$$

Equation 28 is clearly convergent as $n_D \rightarrow \infty$, so that the upper limit in the sum can be extended to infinity if needed. We find that $\Delta(T)$ can be calculated accurate to five decimal places with $n_D = 20$ near T_c and with $n_D = 150$ at low temperatures. To solve eq. 28 numerically, we supply an initial guess for $\Delta(T)$ at a given temperature, test whether it satisfies eq. 25 and update it by the method of golden section (11). The procedure is repeated until the desired accuracy is obtained. The empirical relation

$$\Delta^2(\tau) = \Delta_0^2 \left\{ 1 - a(\tau) \tau^{\eta(\tau)} \exp[b(\tau)(\tau-1)/\tau] \right\} \quad , \quad (29)$$

with

$$a(\tau) = [1.538 + 1.077\tau^2(\tau-1.5)]^{-1} \quad , \quad \eta(\tau) = [2 + 2\tau^2(\tau-1.5)]^{-1}$$

and

$$b(\tau) = [0.5669 + 0.2468\tau^{3.33}(\tau-1.3)]^{-1} \quad ,$$

where $t = T/T_c$, provides a good initial guess, as well as yielding proper values for the gap and its temperature derivative at the limits $t = 0$ and $t = 1$.

In order to find $F_S - F_n$ in the imaginary-time representation, eq. 18 is convenient, since the $\tanh(E_k/2T)$ function can be expressed in terms of $f(E_k)$, as before. Carrying out the analytic continuation first using eq. 23 and then performing the integration with respect to Δ , we get

$$F_n - F_S = N(0) \left\{ -\Delta^2 \ln(t) + 4\pi T \sum_{n=0}^{n_D} [(|\Delta|^2 + \omega_n^2)^{1/2} - \omega_n - |\Delta|^2 (2\omega_n)^{-1}] \right\} . \quad (30)$$

Again, we see that as $n_D \rightarrow \infty$ (i.e., $\omega_n \rightarrow \infty$), the sum inside the square bracket is convergent. The Matsubara representation of the entropy S and the specific heat C_s (at constant volume) are related to the free energy through $S = -(\frac{dF}{dT})$, $C_s = T(\frac{dS}{dT})$ and can be readily obtained from eq. 30 by noting that both Δ and ω_n depend on temperature. In practice, however, we have found that $F_n - F_S$, S and C_s are most easily obtained by first evaluating the free energy through eq. 30 followed by single and double numerical differentiation of $F_n - F_S$ to obtain the entropy and the specific heat (apart from the factors in front).

The formulae given in this section provide an easy numerical scheme to calculate the gap and thermodynamic quantities for a BCS superconductor and should be useful for students and teachers alike. We would also like to point out to those who are interested in more advanced topics that the imaginary-time method can be extended to handle more complex situations,

such as the evaluation of position-dependent energy gaps (12) which occur when a bulk superconductor is in contact with a thin film of normal metal (called a proximity junction) or in situations in which an external current is passed through such a junction (13).

Limitations and Extensions

The BCS theory is based on a simple intuitive model for the effective attractive interaction between electrons, given in eq. 2. In that equation it was assumed that the interaction potential is attractive for wave vectors k which lie within a small spread of $\pm\Delta k$ around the Fermi wave vector k_F and that the potential is ≥ 0 otherwise. In addition, the Debye energy ω_D is assumed to be much larger than the energy ξ_k of the electrons. This approximation is called the "weak-coupling" limit, and many superconductors fall into this category. However, there are superconductors for which the electron-phonon coupling is strong, requiring the BCS theory to be modified. This is done in the "strong-coupling" theory of Eliashberg, which utilizes the fact that the electron-phonon interaction is not instantaneous, but rather is delayed in time (retardation). For details of this theory we refer the reader to the book by Mahan (14). Other applications and extensions of the BCS ideas can be found in the excellent two-volume set edited by R. D. Parks (15). It should be mentioned here that a strong-coupling, phonon-mediated model has been proposed to explain the properties of the new "high- T_c " superconductors (16). However, this model deviates from BCS theory in that the primary charge carriers are bosons (integral spin) rather than fermions.

The BCS theory is a microscopic theory which starts from the basic idea of an attractive interaction between electrons in the presence of a

Fermi sea. Before the microscopic theory was conceived, macroscopic theories based on physical intuition were developed. The most notable and successful of these phenomenological theories is due to Ginzburg and Landau (3). This theory asserts that there exists a complex order parameter $\psi(\mathbf{r})$ (not to be confused with eq. 1) whose square modulus $|\psi(\mathbf{r})|^2$ represents the local density of the superconducting electrons. The order parameter $\psi(\mathbf{r})$ is zero in the normal state ($T > T_c$) and is non-zero in the superconducting state ($T < T_c$). Ginzburg and Landau assumed that the free energy of a superconductor can be expanded in powers of $\psi(\mathbf{r})$ and its gradient $\vec{\nabla}\psi(\mathbf{r})$; symmetry limits the kind of terms in the expansion. It was shown by Gorkov that the BCS theory of superconductivity gives a free-energy expansion which is equivalent to the Ginzburg-Landau equation at temperatures close to T_c .

As mentioned earlier, the BCS theory assumes that the bound electron pairs are in a spin-singlet ($S=0$), even-parity, s-wave ($l=0$) state. Extensions of this theory have been proposed where this limitation has been lifted. For a triplet state ($S=1$), the spins of the electron pair have the same magnetic-moment projections (i.e., the spin wave function is symmetric), and antisymmetry of the total pair wave function requires that parity of its angular momentum part be odd (for example, $l=1$). A triplet p-wave state would exhibit magnetic behavior and has a richer phase diagram than an s-wave state. It has been proposed recently that p-wave pairing might occur in "heavy-fermion" materials (17). Liquid ^3He exhibits a superfluid transition at extremely low temperatures (at about 3 mK) which is associated with triplet p-wave pairing. The theory of superfluidity in ^3He can be described as an extension of the ideas of Balian and Werthamer (14) and is formally similar to the BCS theory.

As another example of the extension of the ideas of the BCS theory, consider the spin-singlet, d-wave ($\ell=2$) pair state, which also has been proposed for the "heavy-fermion" superconductors. The present authors have developed a systematic symmetry analysis to obtain a Ginzburg-Landau free-energy expansion for these even-parity superconducting states (18,19) which enables the calculations of thermodynamic quantities for the heavy-fermion and other unconventional superconductors. A preliminary application of this approach to model the effect of anisotropy in the new "high-temperature" superconductors has also been pursued with some measure of success (20). The extension of the formal BCS theory to model these materials has, however, been met with criticism. Two major premises of BCS theory do not appear valid for these materials. First, the major pairing mechanism is thought to arise from a magnetic interaction rather than a phonon interaction (21-24). This effect could be incorporated into a BCS-like theory through the introduction of an effective, magnetic coupling constant $g_m > 0$ if it were not for the short range of this interaction. It should be recalled that the BCS-theory is a mean-field theory, the second major premise, and consequently it ignores the local variations in the magnetic interaction which appear to be important in the "high- T_c " superconductors. However, in spite of its limitations, BCS theory continues to be the standard in the field and should be understood before other, more elaborate theories can be studied.

VI. CONCLUSIONS

In this paper we have attempted to provide a concise reference source on the basic concepts and computational methods of BCS theory of superconductivity. It is our hope that it will provide the incentive for,

and be helpful in the introduction of BCS theory into the advanced undergraduate or first-year graduate curriculum. The material on thermodynamic properties are intended to provide the reader with the important analytical formulae describing the thermodynamic properties of the superconducting state as well as supply a means of access to the more advanced literature. The simplicity of performing calculations in the imaginary-time formalism should be a valuable aid to getting "hands-on" experience in BCS theory.

APPENDIX

Here we present the limiting forms of the thermodynamic functions for a superconductor with gap $\Delta(T)$ at low temperature ($T \rightarrow 0$) and at high temperature ($T \approx T_c$). We also give some additional mathematical formulae which serve as useful checks on the numerical results obtained from real-time representation formulae.

Case (1) $T \rightarrow 0$

As $T \rightarrow 0$, the order parameter $\Delta \approx \Delta_0$ and is approximately independent of T . The leading deviation from Δ_0 is exponential in nature (12), indicating the existence of an energy gap of the form

$$\Delta^2 \approx \Delta_0^2 [1 - \sqrt{8\pi T/\Delta_0} \exp(-\Delta_0/T)] \quad . \quad (A1)$$

Similarly (12),

$$F_s - F_n = (\pi^2/3)T^2N(0) - N(0)[\frac{1}{2}\Delta^2 + \sqrt{2\pi\Delta_0^3}T \exp(-\Delta_0/T)] \quad , \quad (A2)$$

$$S_s \approx 2N(0)(2\pi\Delta_0^3/T)^{1/2} \exp(-\Delta_0/T) \quad , \quad (A3)$$

and

$$\begin{aligned} C_s(T)/(\gamma T_c) &= C_s(T)/C_n(T_c) \\ &\approx (6/\pi^2) \sqrt{(\pi/2)(\Delta_0/T)^3 (\Delta_0/T_c)} \exp(-\Delta_0/T) \quad , \end{aligned} \quad (A4)$$

with $\gamma = 2\pi^2 N(0)/3$.

The exponential term in the specific heat is again indicative of an energy gap in the excitation spectrum. Equation A4 can be easily obtained from eq. 21 by noting that the temperature derivatives are zero and that we can use the asymptotic form of the modified Bessel function (since $\Delta_0/T \rightarrow \infty$),

$$K_\nu(x) \xrightarrow{x \rightarrow \infty} [\pi/(2x)]^{1/2} \exp(-x) \quad . \quad (A5)$$

Case (2) $T \approx T_c$

Close to T_c , $\Delta(T)$ is vanishingly small and serves as a small expansion parameter. Noting that near T_c , $Y(t) \rightarrow 1 - 2(1-t)$, we get

$$\Delta^2 \approx 8\pi^2 [7\zeta(3)]^{-1} T_c^2 (1-t) \quad , \quad \zeta(3) = 1.202 \quad , \quad (A6)$$

$$F_s - F_n \approx -4 N(0) [7\zeta(3)]^{-1} (\pi T_c)^2 (1-t)^2 \quad , \quad (A7)$$

$$S_s = -8N(0)[7\zeta(3)]^{-1} (\pi T_c)^2 (1-t) + S_n, \quad (A8)$$

where $S_n = (2\pi^2/3)N(0) T$,

and

$$\frac{C_s(T_c)}{C_n(T_c)} - 1 = \frac{12}{7\zeta(3)} = 1.426. \quad (A9)$$

Note that the RHS of eq. A9 gives the jump in the specific heat at T_c . The term -1 on the LHS of eq. A9, which comes from the nonsuperconductor contribution, is obtained by using the asymptotic form

$$K_\nu(x) \xrightarrow{x \rightarrow 0} \frac{\nu!}{2} \left(\frac{2}{x}\right)^\nu$$

$$\text{and the sum } \sum_{n=0}^{\infty} (-1)^n (n+1)^{-2} = \pi^2/12.$$

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